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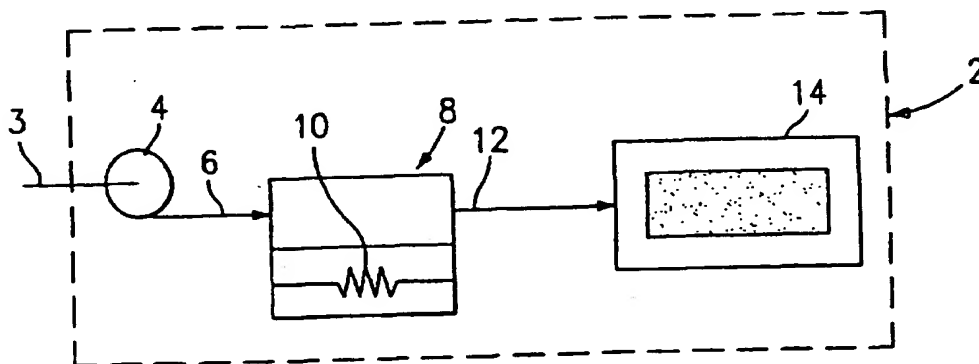
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(54) Title: METHOD FOR DESULFURIZING GASOLINE OR DIESEL FUEL FOR USE IN AN INTERNAL COMBUSTION ENGINE



(57) Abstract: A fuel processing method which is operable to remove substantially all of the sulfur present in an undiluted oxygenated hydrocarbon fuel stock supply which contains an oxygenate and which is used to power an internal combustion engine (14) is disclosed. The undiluted hydrocarbon fuel supply is passed through a nickel reactant desulfurized bed (8) wherein essentially all of the sulfur in the organic sulfur compounds reacts with the nickel reactant, and is converted to nickel sulfide, while the desulfurized organic remnants continue through the remainder of the fuel processing system. The method can be used to desulfurize either a liquid or a gaseous fuel system, which contains an oxygenate such as MTBE, ethanol, methanol, or the like.

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**METHOD FOR DESULFURIZING GASOLINE OR DIESEL FUEL FOR USE  
IN AN INTERNAL COMBUSTION ENGINE**

**Technical Field**

The present invention relates to a method and system for desulfurizing gasoline, diesel fuel or like hydrocarbon fuels so as to reduce the sulfur content of the fuel and render the fuel more desirable for use in a mobile vehicular internal combustion engine. More particularly, the desulfurizing method and system of this invention are operable to reduce the amount of organic sulfur compounds found in gasoline to levels which will not cause undue corrosion to engine and exhaust components. Another advantage to use of the sulfur-depleted gasoline fuel is the increased efficiency and useful life of the catalytic converters used to scrub IC engine exhaust. The method of this invention involves the use of a nickel reactant bed which has an extended useful life cycle due to the presence of oxygenates such as alcohols, water, or other compounds in the fuel stream.

**Background Art**

Gasoline, diesel fuel, and like hydrocarbon fuels are useful as a fuel for internal combustion engines, despite the existence of relatively high levels of naturally-occurring complex organic sulfur compounds in the gasoline or diesel fuel. The sulfur compounds are undesirable since they are known to cause corrosion damage components of the internal combustion engine system, such as engine cylinder walls and exhaust system walls when the fuel is combusted. As noted above, catalytic converter performance is also adversely effected. The sulfur compounds in the aforesaid fuels are also undesirable since they are converted to sulfur dioxide ( $\text{SO}_2$ ) when the fuel is combusted. It is well known that  $\text{SO}_2$  and  $\text{SO}_3$  when exhausted into the atmosphere will cause "acid rain" due to its subsequent conversion to  $\text{H}_2\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  in the ambient atmosphere. The former problem of engine damage has not been addressed in any fashion, other than by attempting to reduce the amount of sulfur in the gasoline or diesel fuel during the refining process. This solution also helps ameliorate the exhaust problem, but the

acceptable amount of sulfur compounds in gasoline or diesel fuel can vary from one locale to the next in accordance with local environmental regulations. At the present time, in the United States of America, the State of California has the most stringent requirements for fuel sulfur content, which is about 30 ppm sulfur in the fuel. Even with this low concentration of sulfur in the fuel, engine damage and decreased catalytic converter performance can still result.

An article published in connection with the 21st Annual Power Sources Conference proceedings of May 16-18, 1967, pages 21-26, entitled "Sulfur Removal for Hydrocarbon-Air Systems", and authored by H. J. Setzer et al, relates to the use of fuel cell power plants for a wide variety of military applications.

It would be highly desirable from an environmental standpoint to be able to power vehicles, such as an automobile with a low sulfur fuel, such as a low sulfur gasoline or diesel fuel. In order to provide such a vehicular power source, the amount of sulfur in the processed fuel gas would have to be reduced to and maintained at less than about 0.05 parts per million. The desulfurized fuel can be used as a fuel for an internal combustion engine. The fuel being processed can be gasoline or diesel fuel, or some other fuel which contains relatively high levels of organic sulfur compounds such as thiophenes, mercaptans, sulfides, disulfides, and the like. The fuel stream is passed through a nickel reactant desulfurizer bed wherein essentially all of the sulfur in the organic sulfur compounds reacts with the nickel reactant and is converted to nickel sulfide leaving a desulfurized hydrocarbon fuel.

We have discovered that desulfurization of a gasoline or diesel fuel which uses a nickel catalytic adsorbent bed cannot be performed over a significantly extended period of time, unless the fuel includes an oxygenate compound in appropriate proportions, a small amount of added water, preferably in the form of steam, or a small amount of added hydrogen. Various oxygenates which could suffice for the desulfurization process include MTBE, ethanol or other alcohols, ethers, or the like.

### Disclosure of the Invention

This invention relates to an improved method for processing a gasoline, diesel, or other hydrocarbon fuel stream over an extended period of time, which method is operable to remove substantially all of the sulfur  
5 present in the fuel stream.

Gasoline, for example, is a hydrocarbon mixture of paraffins, naphthenes, olefins and aromatics, whose olefinic content is between 1% and 15 %, and aromatics between 20 % and 40%, with total sulfur in the range of about 20 ppm to about 1,000 ppm. The national average for the United  
10 States is 350 ppm sulfur. The legally mandated average for the State of California is 30 ppm sulfur. As used in this application, the phrase "California Certified Gasoline" refers to a gasoline which has between 30 and 40 ppm sulfur content and which contains about 11% by volume MTBE at the present time. California Certified Gasoline is used by new car manufacturers to  
15 establish compliance with California emissions certification requirements.

We have discovered that the presence of oxygenates in the gasoline, like MTBE (methyl-tertiary-butyl ether, i.e.,  $(\text{CH}_3)_3\text{COCH}_3$ ), ethanol, or water vapor for example, will prevent rapid deactivation of the nickel catalytic adsorption of organic sulfur compounds from the fuel stream. Ethanol could  
20 be an appropriate solution to this problem since it is non-toxic, is not a carcinogen, and is relatively inexpensive and readily available in large supplies as a byproduct of the agriculture industry. Methanol, which would also extend the desulfurizer bed life, is not preferred since it is toxic; while MTBE is likewise not preferred since it is thought to be a carcinogenic  
25 compound, and may be banned in certain areas of the United States in the near future by new environmental regulations. Preferred oxygenates are non-toxic and non-carcinogenic oxygen donor compounds, such as ethanol, water vapor, or the like.

The effectiveness of a nickel adsorbent reactant to adsorb organic  
30 sulfur compounds from gasoline depends on the relative coverage of the active reactant sites by adsorption of all the various constituents of gasoline. In other words, the catalytic desulfurization process depends on the amount of competitive adsorption of the various constituents of gasoline. From the adsorption theory, it is known that the relative amount of adsorbate on an

adsorbent surface depends primarily on the adsorption strength produced by attractive forces between the adsorbate and adsorbent molecules; secondarily on the concentration of the adsorbate in the gasoline, and temperature. Coverage of a reactant surface by an adsorbate increases with increasing attractive forces; higher fuel concentration; and lower temperatures. Saturated hydrocarbons only physically adsorb onto the nickel reactant surface at temperatures which are less than about 100°F (37.8°C) therefore paraffins, and most likely naphthenes, won't compete with sulfur compounds for adsorption sites on the nickel reactant at temperatures above about 250°F (121.1°C) and 300°F (148.9°C).

On the other hand, unsaturated hydrocarbons, such as aromatics and olefins, adsorb largely irreversibly on transition metal surfaces even at room temperature. When an unsaturated hydrocarbon, such as an aromatic or an olefin, adsorbs on a transition metal surface, and the surface is heated, the adsorbed molecules, rather than desorbing intact, decompose to evolve hydrogen, leaving the surface covered by partially dehydrogenated fragments, i.e., tar or coke precursors. We have discovered that, at about 350°F (176.7°C), unsaturated hydrocarbons are nearly completely dehydrogenated, and the dehydrogenated tar fragments form multiple carbon atom-to-nickel reactant surface bonds. This explains why aromatics and olefins in gasoline, in the absence of oxygenated compounds in appropriate concentrations, will deactivate the nickel reactant from adsorbing sulfur after a relatively short period of time.

In general, the adsorption strength of a compound depends on the dipole moment, or polarity, of the molecule. A higher dipole moment indicates that the compound is more polar and is more likely to adsorb on a reactant surface. Aromatics are an exception to this rule because their molecular structure includes a  $\pi$  ring of electron forces that produces a cloud of induced attractive forces with adjacent surfaces. Based on the dipole moments of hydrocarbons, allowing for the  $\pi$  ring in aromatics, the order of adsorption strength (highest to lowest) is: nitrogenated hydrocarbons > oxygenated hydrocarbons > aromatics > olefins > hydrocarbons containing sulfur > saturated hydrocarbons. Since the adsorption strength of the oxygenated hydrocarbons (such as ethanol, methanol, MTBE, or the like) is

greater than that for aromatics and olefins, oxygenated hydrocarbons, or other oxygen donor compounds, if present in the gasoline or diesel fuel being desulfurized, will provide greater coverage of the nickel reactant sites than do the aromatics and olefins in the gasoline. Thus, the oxygenated

5 hydrocarbons can reduce the adsorption of aromatics and olefins on the nickel reactant bed. Although saturated hydrocarbons (paraffins and cycloparaffins) would not be expected to be adsorbed on the desulfurization nickel reactant to a significant extent, oxygenated hydrocarbons will also prevent them from adsorbing onto the nickel reactant.

10 We have also discovered that the adsorbed oxygenated hydrocarbons do not inhibit the sulfur compounds from being adsorbed on the nickel reactant. The oxygenated hydrocarbons and the sulfur compounds are both quite polar and therefore they are miscible, which allows the sulfur compounds to dissolve into and diffuse through the adsorbed layer of

15 oxygenated hydrocarbons to the active nickel metal reactant sites. Thus, the oxygenated hydrocarbons provide a "shield" which inhibits the carbon-forming hydrocarbons from contacting the nickel reactant sites while allowing the sulfur compounds to contact and react with the active nickel metal reactant sites.

20

### **Brief Description of the Drawings**

Fig. 1 is a graph of the result of a short (seven hour) desulfurizer bed test run with three different modified formulations of California Certified Gasoline, with the ordinate showing the sulfur level in parts per million (ppm) at the reactant bed exit for the various gasoline formulations, versus the test

25 run operating time in hours shown on the abscissa;

Fig. 2 is a graph of the results of a longer desulfurizer bed test run (about four hundred eighty five hours) with unmodified California Certified Gasoline, with the ordinate showing the sulfur level in the gasoline in ppm at the nickel reactant bed exit, versus the operating time in hours shown on the

30 abscissa;

Fig. 3 is a graph of the results of the same desulfurizer bed test run shown in Fig. 2, but with the ordinate showing the oxygenate level in the

gasoline, in percent by weight, at the reactant bed exit, versus the test run operating time in hours shown on the abscissa;

Fig. 4 is a graph of the result of a desulfurizer bed test run with a commercially available gasoline, with the ordinate showing the sulfur level in ppm at the nickel reactant bed exit versus the operating time of the desulfurizer in hours shown on the abscissa;

Fig. 5 is a graph of the result of several different duration desulfurizer bed test runs using different modified formulations of California Certified Gasoline, one with, and one without oxygenates, with the ordinate showing the carbon level (in percent by weight) which was deposited on the reactant in each of the successive desulfurizer reactor sections of the desulfurizer, as shown on the abscissa, at the end of the test runs;

Fig. 6 is a graph of the sulfur content of the exit stream of a desulfurized gasoline fuel stream over a period of time at varied operating temperatures, when a small amount of water is present, and when no water is present, in the fuel stream, with the ordinate showing sulfur content in ppm and the abscissa showing operating time in hours;

Fig. 7 is a graph where the ordinate shows the operating temperatures in degrees Fahrenheit/degrees Celsius of the system described in Fig. 6 over the same period of time; and

Fig. 8 is a schematic view of an embodiment of the gasoline desulfurizer system of this invention, which desulfurizes gasoline on board a vehicle whose engine is powered by the desulfurized gasoline.

### **Modes for Carrying Out the Invention**

Referring now to the drawings, Fig. 1 is a graph of the results of relatively short desulfurizer test runs using various formulations of California Certified Gasoline. The ordinate shows the sulfur level in ppm for the various formulations at the reactant bed exit. The abscissa shows the operating time of the test runs in hours. In these short term (seven hour) test runs, sulfur was added to all of the California Certified Gasoline formulations, so that the gasoline contained 240 ppm of sulfur. One of the gasoline formulations contained 11% MTBE by volume, which is an oxygenate and which is presently a conventional component of California Certified Gasoline; another

of the formulations contained 10% ethanol by volume, which is also an oxygenate; and the third formulation contained essentially no oxygenate. In each of the test runs, the gasoline was run through a nickel reactant bed so as to attempt to remove sulfur from the gasoline. The trace line A shows the sulfur content of the gasoline formulation which did not contain an oxygenate. The sulfur content was measured at the exit end of the desulfurizer reactant bed. Trace A clearly shows that the oxygenate-free gasoline formulation had a steadily rising sulfur content at the desulfurizer exit during the duration of the test despite being run through the desulfurizer reactant bed indicating deactivation of the desulfurization reactant. Trace B shows the sulfur content of the gasoline formulation which contained MTBE. Trace C shows the sulfur content of the gasoline formulation which contained ethanol. This graph shows a major improvement and a decrease in sulfur at the reactant bed exit, when an MTBE or ethanol oxygenate is contained in the gasoline. This graph shows that the oxygenate component of the gasoline prolongs the ability of the reactant bed to remove sulfur from the gasoline.

Fig. 2 is a graph of the results of a longer desulfurizer test run using California Certified Gasoline which contained about 30 ppm sulfur and about 11% MTBE by volume. The ordinate shows the sulfur level in ppm at the exit of the reactant bed, and the abscissa shows the operating time in hours. The test was run until sulfur breakthrough occurred. The goal of the desulfurizer is to maintain the sulfur content of the gasoline below about 0.05 ppm so that the gasoline will be eminently suitable for fueling an internal combustion engine. It will be understood that, "sulfur breakthrough" is defined by our requirements as occurring when a sustained post-reactant bed sulfur content of greater than about 0.05 ppm is present in the desulfurized gasoline. The trace D shows the sulfur level in ppm at the exit of the reactant bed versus the operating time in hours and shows that the desulfurizer operated successfully for about 400 hours with consistent sulfur levels in the nickel reactant bed exit stream of below 0.05 ppm. In this test run, the long term benefit of using an oxygenate in the fuel to minimize sulfur penetration through the desulfurizer device is demonstrated.

Fig. 3 is a graph of the results of the same longer term desulfurizer test run shown in Fig. 2. In Fig. 3, the ordinate shows the oxygenate level by



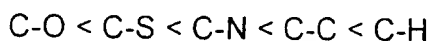
percent weight at the nickel reactant bed exit and the abscissa shows the operating time in hours. From this figure, it will be noted that when the nickel reactant bed can no longer decompose the oxygenate, the nickel reactant loses its ability to remove organic sulfur compounds. It is noted from trace E in Fig. 3 that at about 400 hours, the MTBE content of the fuel exiting the nickel reactant bed was about 11% by volume which is the same concentration of MTBE in the gasoline entering the nickel reactant bed. Note that early in the test run, the nickel reactant bed is more capable of decomposing the MTBE, but this ability gradually declines as the test run continues. This inability to decompose the oxygenate results in an increase in the sulfur content at the nickel reactant bed exit, as shown in Fig. 2.

Fig. 4 is a graph of the results of another longer term desulfurizer test run using a gasoline which had about a 90 ppm sulfur content and which contained about 11% MTBE by volume. The ordinate shows the sulfur level in ppm and the abscissa shows the operating time in hours. Trace F shows that the sulfur level at the nickel reactant bed exit remained below 0.05 ppm for about 125-135 hours, after which sulfur breakthrough occurred. In this test run, the long term benefit of using oxygenates in the fuel to minimize sulfur getting through the desulfurizing bed is also demonstrated.

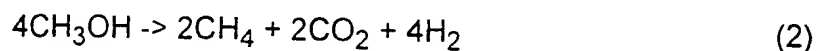
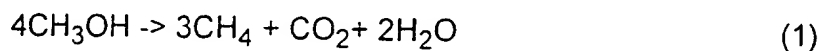
Fig. 5 is a graph showing the results of two desulfurizer test runs using two different formulations of California Certified Gasoline, one containing an oxygenate (MTBE, 11% by volume), and the other containing no oxygenate. The ordinate shows the carbon level by percent weight, deposited in each of the successive sections of the desulfurizer nickel reactant bed shown on the abscissa. In this figure, the post test carbon content for successive sections of the desulfurizers was measured and is shown for two tests that were run for different time periods, both of which were run until sulfur breakthrough occurred. Trace H shows the results of the test run for the gasoline formulation that contained no oxygenate. This test was run for 60 hours at which point in time, sulfur breakthrough occurred. Trace G shows the results of the test run for the gasoline formulation that contained MTBE. This test was run for 485 hours at which point in time, sulfur breakthrough occurred. It was noted that the presence or absence of the oxygenate in the gasoline

being processed did not effect the carbon build up profile on the nickel reactant bed, but it did increase the time period which is needed to reach the sulfur breakthrough point in terms of carbon deposition. In each test, the degree of carbon build up on the nickel reactant at the sulfur breakthrough point in each section of the desulfurizer is almost exactly the same. This figure demonstrates that "sulfur breakthrough" is a function of the extent of carbon deposition on the nickel reactant bed, and is not a function of the extent of sulfur removal by the nickel reactant bed. This figure also demonstrates that the addition of oxygenates to the gasoline retards carbon deposition on the nickel reactant bed, and thus enables extended sulfur removal from the fuel stream by the nickel reactant bed.

At this stage, we conclude that the presence of oxygenates in the gasoline or other fuel maintains the desulfurization activity of the nickel reactant by significantly suppressing the carbon deposition (coke deposits and strongly adsorbed species), and by keeping the nickel reactant active sites clean and available for desulfurization of the S-containing organic molecules. As was mentioned before, this could be achieved by an in situ formation of hydrogen and/or water vapor due to the MTBE decomposition process (chemical reaction effect). Therefore, we propose that MTBE, and for the same reason other oxygenated organic molecules, are strongly adsorbed on the Ni surface due to their high dipole moment where they decompose to isobutylene and methanol. The adsorbed oxygenate decomposes because the nickel reactant is very active and the C-O bond is easily broken. In general, the order in the required energy to break a C-X bond is:



A nickel reactant promotes the formation of methanol, a byproduct of MTBE decomposition, or ethanol disproportionation reaction. When methanol is decomposed, the following reactions occur:



For ethanol, the same reactions should produce ethane instead of methane. The presence of water vapor or hydrogen suppresses carbon formation, especially at elevated temperatures. The hydrogen produced on the nickel reactant bed by equation (2) will hydrogenate carbon precursors emanating from the desulfurized organic sulfur components, and from the adsorbed/decomposed olefins and aromatics in the gasoline, through reaction with hydrogen emanating from the desulfurized fuel gas (Ely-Rideal mechanism) or through hydrogen spill over. Hydrogenation of carbon precursors from sulfur compounds, olefins and aromatics could occur entirely on the nickel reactant surfaces from spill over of hydrogen generated by decomposition of the MTBE without initiating hydrogen exchange with the fuel gas stream. "Spill over" is the surface migration of hydrogen atoms from the nickel reactant site(s) that produce the hydrogen in equation (2) to the site(s) that adsorb the olefins and aromatics.

The formation of hydrogen is demonstrated in Table 1 (below), which shows the decrease in olefin level during the desulfurization process for the same commercially available gasoline containing MTBE shown in Fig. 4. Apparently, the hydrogen provided by decomposition of MTBE serves to hydrogenate the olefins thereby forming saturated paraffins. It is apparent from Table 1 that the decomposition of MTBE not only generates hydrogen, but also catalyzes the dehydrogenation of naphthenes to generate aromatics and more hydrogen.

Table 1 is a "PONA" (which is an acronym for paraffins, olefins, naphthene, and aromatics) analysis of the changes in PONA compounds which are found in the gasoline described in Fig. 4, both before and after desulfurization; and also of the change in the sulfur content of the gasoline.

**Table 1**

Hydrocarbon Type	Before Desulfurization	After Desulfurization
Paraffins	38.8%	41.1%
Olefins	14.9%	12.6%
Naphthenes	9.6%	5.8%
Aromatics	36.7%	40.6%

Sulfur

90 ppm

&lt;0.05 ppm

Table 2 shows that, without MTBE, there is essentially no change in the "PONA" percentages in a low sulfur content, commercially available gasoline which is passed through the desulfurization nickel reactant bed. Also, Table 2 demonstrates that the sulfur content of the low sulfur content gasoline still contains an unacceptably high content of sulfur after the desulfurization step.

**Table 2**

	Hydrocarbon Type	Before Desulfurization	After Desulfurization
	Paraffins	64.6%	64.50%
10	Olefins	3.7%	3.65%
	Naphthenes	2.89%	2.82%
	Aromatics	28.8%	29.00%
	Sulfur	30.9 ppm	1.00 ppm

Desulfurization of a gasoline fuel sample containing about 30 ppm sulfur was carried out at a temperature of 375°F (190.6°C). Fig. 6 shows the exit stream desulfurization history of this low sulfur gasoline fuel sample. In Fig. 6 the ordinate shows the desulfurization test run was run at a temperature of 375°F (190.6°C), except for the time period between 73 and 120 hours. During that time period, the reaction temperature was lowered to 350°F (176.7°C), as shown in Fig. 7. At the 375°F (190.6°C) operating temperature, the fuel stream exiting the desulfurizer nickel reactant bed contained about 1% to about 2% water condensate which was derived from the MTBE. At the operating temperature of 350°F (176.7°C), the exiting fuel stream did not contain any obvious water condensate. This fact confirms the formation of water, and coextant superior desulfurization results obtained when water is present in the fuel stream. It is noted from Fig. 6, that after the operating temperature is lowered to 350°F (176.7°C), and the water condensate in the fuel stream disappears, the sulfur level in the exiting fuel stream begins to rise, and then, sometime after the operating temperature is

increased, and the water condensate reappears in the fuel stream, the sulfur level in the exiting fuel stream subsides.

Fig. 8 shows an embodiment of the desulfurization system of this invention wherein the desulfurizing bed 8 is positioned onboard a vehicle 2.

5 The system includes a fuel line 3 from the vehicle gas tank to a pump 4 which pumps the fuel through a line 6 to the desulfurizer bed 8. The bed 8 is heated to operating temperatures by an electric heater 10. The desulfurized gasoline passes from the desulfurizing bed 8 through a line 12 to the internal combustion engine 14 where it is combusted.

10 We have determined that the oxygenate not only protects the nickel reactant metal surface with an oxygenate "shield", it also produces hydrogen and water which enables the metal surface to remain free of excessive carbon deposits for longer periods of time than if no oxygenate were present. The addition of very small quantities of water in the fuel stream at the  
15 desulfurizer bed inlet, has been shown to provide the same quantity of water and hydrogen as is produced from the use of MTBE.

As a result, the MTBE could be eliminated from the gas stream when a vaporized water stream is utilized. Minimal amounts of water oxygenate can be employed, contrary to the teachings of aforementioned Setzer et al article  
20 which was published in the 21st Annual Power Sources conference proceedings, which article requires the use of three pounds of water for one pound of fuel in order to reform the fuel gas stream. The operating temperature range of 325°F - 450°F (162.8°C - 232.2°C) for liquid fuels, and 250°F - 450°F (121.2°C - 232.2°C) for gaseous fuels available in  
25 performance of this invention, both of which are below the temperature range suggested in the prior art for the performance of the prior art hydrodesulfurization processes.

It will be readily appreciated that the inclusion of an effective amount of an oxygenate, or water in a sulfur-containing fuel, such as gasoline, will allow  
30 sulfur to be removed from the fuel to the extent necessary to provide a low sulfur content fuel, i.e., less than about .05 ppm sulfur, for fueling an internal combustion engine. The sulfur compounds are removed from the raw fuel by means of a nickel reactant bed through which the fuel flows prior to entering the internal combustion engine. The oxygenate addition also serves to

control carbon deposition on the nickel reactant bed thereby extending the nickel reactant bed's useful life and enhancing the sulfur removal capabilities of the nickel reactant bed. The desulfurization process can be performed inside of the vehicle, in the service station fuel pumping apparatus, or at the  
5 fuel refinery.

CLAIMS

1. A method for desulfurizing a hydrocarbon fuel stream so as to convert the hydrocarbon fuel stream into a low sulfur content fuel, which low sulfur content fuel is suitable for use in an internal combustion engine, said method comprising the steps of:
  - 5 a) providing a nickel reactant desulfurization station which is operative to convert sulfur contained in organic sulfur compounds contained in the fuel stream to nickel sulfide;
  - b) introducing a hydrocarbon fuel stream which contains an oxygenate into said nickel reactant desulfurization station; and
  - 10 c) said oxygenate being present in said fuel stream in an amount which is effective to provide an effluent fuel stream at an exit end of said nickel reactant station which effluent fuel stream contains no more than about 0.05 ppm sulfur.
2. The method of Claim 1 wherein the oxygenate is selected from the group consisting of water, alcohol, ether, and mixtures thereof.
3. The method of Claim 2 wherein the oxygenate is selected from the group consisting of water, MTBE, ethanol, methanol, and mixtures thereof.
4. The method of Claim 1 wherein said hydrocarbon fuel is gasoline.
5. The method of Claim 1 wherein said hydrocarbon fuel is diesel fuel.

6. A method for desulfurizing a gasoline or diesel fuel stream so as to convert the gasoline fuel stream into a low sulfur content fuel, which low sulfur content fuel is suitable for use in an internal combustion engine, said method comprising the steps of:

- 5       a) providing a nickel reactant desulfurization station which is operative to convert sulfur contained in organic sulfur compounds contained in the fuel stream to nickel sulfide;
- b) introducing a gasoline or diesel fuel stream which contains an oxygenate into said nickel reactant desulfurization station; and
- 10       c) said oxygenate being present in said fuel stream in an amount which is effective to provide an effluent fuel stream at an exit end of said nickel reactant station which effluent fuel stream contains no more than about 0.05 ppm sulfur.

7. The method of Claim 5 wherein the oxygenate is selected from the group consisting of water, alcohol, ether, and mixtures thereof.

8. The method of Claim 7 wherein the oxygenate is selected from the group consisting of water, MTBE, ethanol, methanol, and mixtures thereof.

9. A method for desulfurizing a gasoline or diesel fuel stream so as to convert the fuel stream into a low sulfur content fuel, which low sulfur content fuel is suitable for use in an internal combustion engine, said method comprising the steps of:

- 5       a) providing a nickel reactant desulfurization station which is operative to convert sulfur contained in organic sulfur compounds contained in the fuel stream to nickel sulfide;
- b) introducing a gasoline or diesel fuel stream which contains an oxygenate into said nickel reactant desulfurization station; and
- 10       c) said oxygenate being present in said fuel stream in an amount which is effective to provide a continuous fuel stream at an exit end of said nickel reactant station which continuous fuel stream contains on average no more than about 0.05 ppm sulfur.



10. A method for desulfurizing a gasoline or diesel fuel stream so as to convert the fuel stream into a low sulfur content fuel, which low sulfur content fuel is suitable for use in an internal combustion engine, said method comprising the steps of:

- 5 a) providing a nickel reactant desulfurization station which is operative to convert sulfur contained in organic sulfur compounds contained in the fuel stream to nickel sulfide;
- b) introducing a gasoline or diesel fuel stream which contains an oxygenate into said nickel reactant desulfurization station; and
- 10 c) said oxygenate being converted to isobutylene and methanol by said nickel catalyst in amounts which are effective to inhibit carbon deposition in said nickel catalyst station and provide a continuous fuel stream at an exit end of said nickel reactant station which continuous fuel stream contains no more than about 0.05 ppm sulfur.

11. A method for desulfurizing a gasoline or diesel fuel stream so as to convert the fuel stream into a low sulfur content fuel, which low sulfur content fuel is suitable for use in an internal combustion engine, said method comprising the steps of:

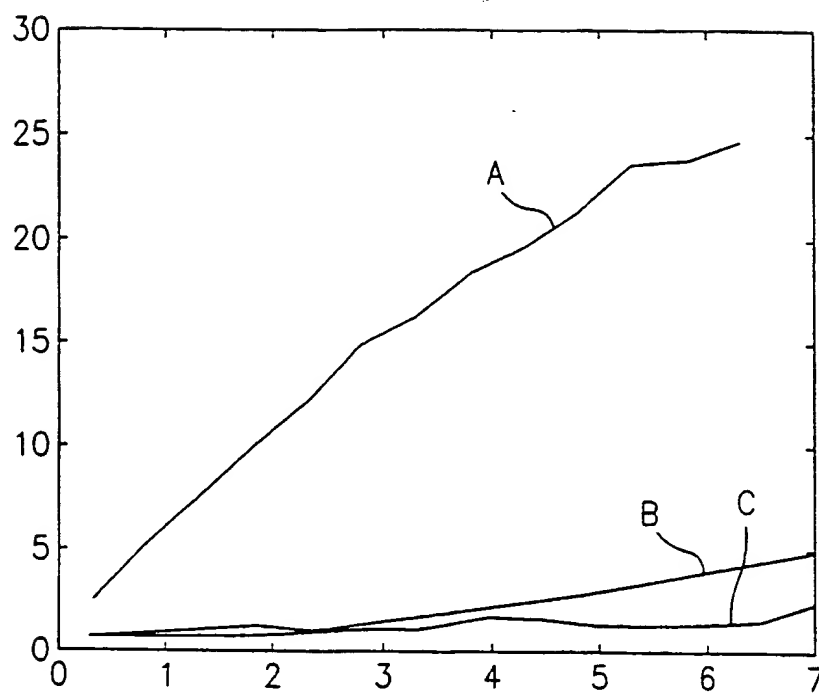
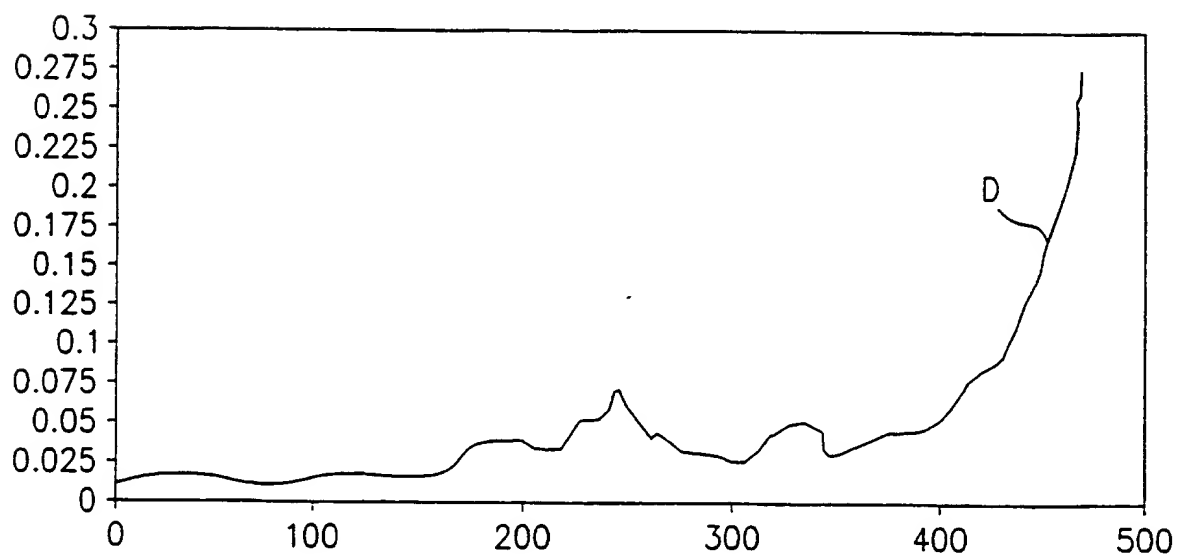
- 5 a) providing a nickel reactant desulfurization station which is operative to convert sulfur contained in organic sulfur compounds contained in the fuel stream to nickel sulfide;
- b) introducing a gasoline or diesel fuel stream which contains an oxygenate into said nickel reactant desulfurization station, said oxygenate
- 10 being present in said fuel stream in an amount which is effective to provide a low sulfur content fuel stream at an exit end of said nickel catalyst station which low sulfur content fuel stream contains no more than about 0.05 ppm sulfur; and
- c) said oxygenate being converted to isobutylene and methanol by said
- 15 nickel reactant during said desulfurizing step, said low sulfur content fuel stream being formed so long as said nickel reactant continues to convert the oxygenate.

12. A method for desulfurizing a liquid gasoline or diesel fuel stream so as to convert the fuel stream into a low sulfur content fuel, which low sulfur content fuel is suitable for use in an internal combustion engine, said method comprising the steps of:

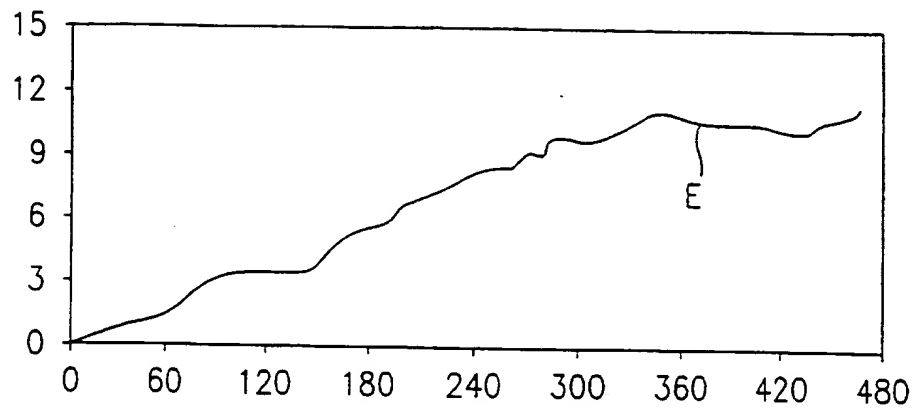
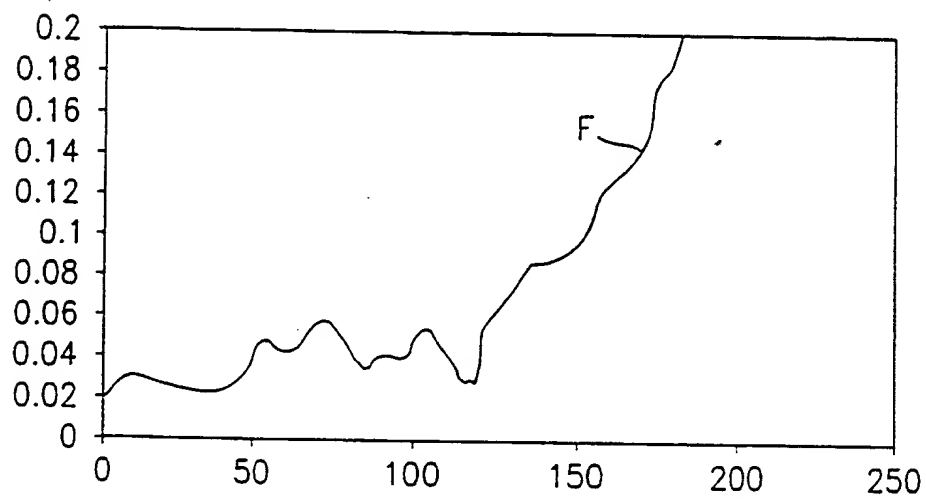
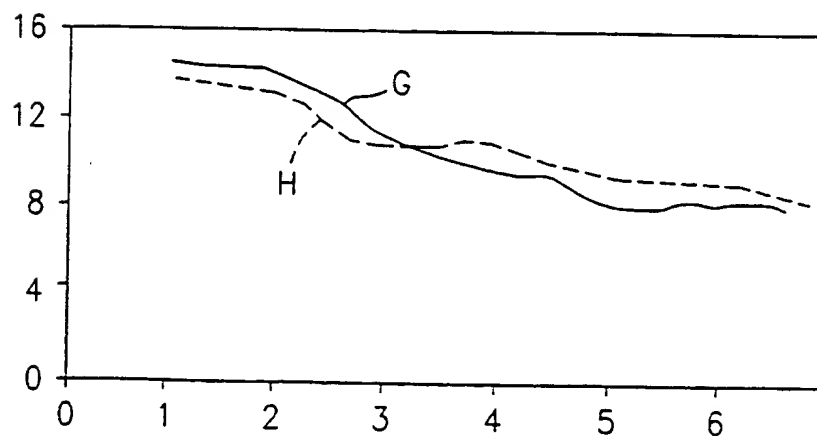
- 5 a) providing a nickel reactant desulfurization station which is operative to convert sulfur contained in organic sulfur compounds contained in the fuel stream to nickel sulfide;
- b) maintaining said nickel reactant desulfurization station at a temperature in the range of about 300°F (149°C) to about 450°F (232°C);
- 10 c) introducing a liquid gasoline or diesel fuel stream which contains an oxygenate into said nickel reactant desulfurization station, said oxygenate being present in said fuel stream in an amount which is effective to provide a low sulfur content fuel stream at an exit end of said nickel reactant station which low sulfur content fuel stream contains no more than about 0.05 ppm
- 15 sulfur; and
- d) said oxygenate being converted to isobutylene and methanol by said nickel reactant during said desulfurizing step, said low sulfur content fuel stream being formed so long as said nickel reactant continues to convert the oxygenate.

13. A method for desulfurizing a liquid gasoline or diesel fuel stream so as to convert the fuel stream into a low sulfur content fuel, which low sulfur content fuel is suitable for use in an internal combustion engine, said method comprising the steps of:
- 5 a) providing a nickel reactant desulfurization station which is operative to convert sulfur contained in organic sulfur compounds contained in the fuel stream to nickel sulfide;
  - b) maintaining said nickel reactant desulfurization station at a temperature in the range of about 300°F (149°C) to about 450°F (232°C);
  - 10 c) introducing a mixture of about 2% to about 5% water and a liquid gasoline or diesel fuel stream, which mixture contains an oxygenate, into said nickel reactant desulfurization station, said oxygenate being present in said mixture in an amount which is effective to provide a low sulfur content fuel stream at an exit end of said nickel reactant station, which low sulfur content
  - 15 fuel stream contains no more than about 0.05 ppm sulfur; and
  - d) said oxygenate being consumed by said nickel reactant during said desulfurizing step, said low sulfur content fuel stream being formed so long as said nickel reactant continues to consume the oxygenate.
14. The method of Claim 13 wherein the water in said mixture is the sole oxygenate in said mixture.
15. The method of Claim 13 wherein the oxygenate includes an alcohol present in said fuel stream.
16. The method of Claim 15 wherein the alcohol is selected from the group consisting of methanol, ethanol, propanol, and mixtures thereof.
17. The method of Claim 13 wherein said oxygenate is an ether.
18. The method of Claim 17 wherein said oxygenate is MTBE.

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*FIG. 1**FIG. 2*

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*FIG. 3**FIG. 4**FIG. 5*

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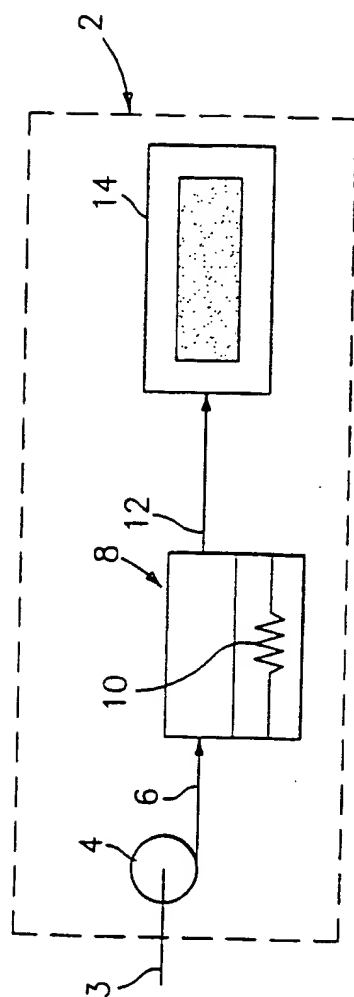


FIG. 8

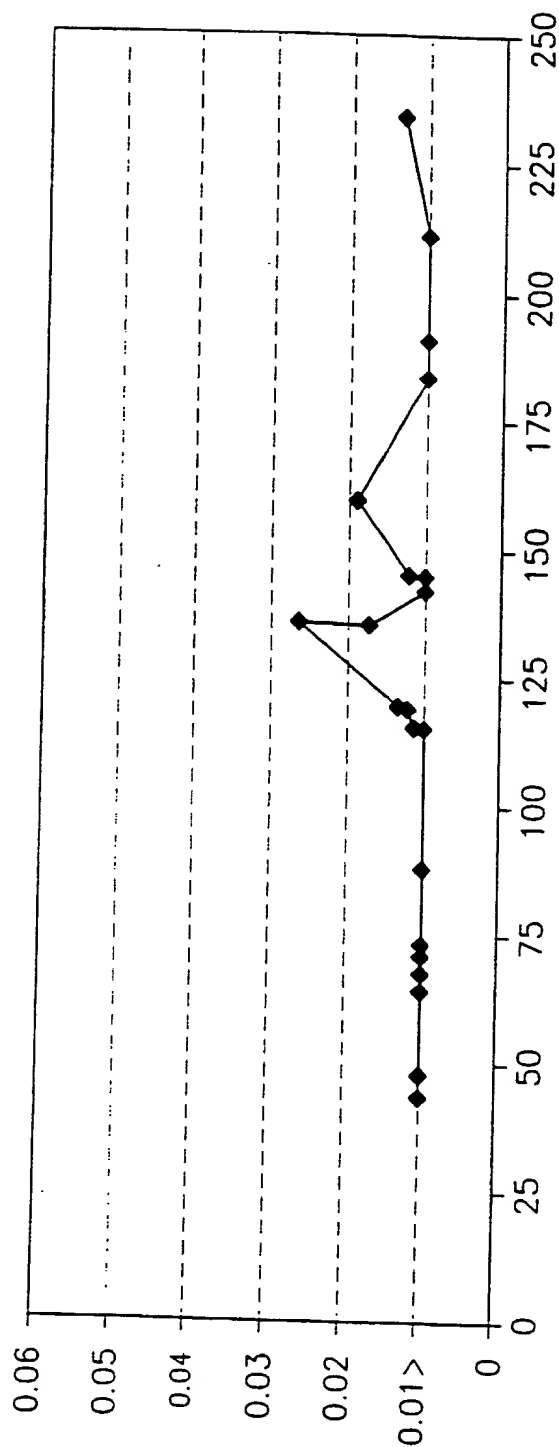


FIG. 6

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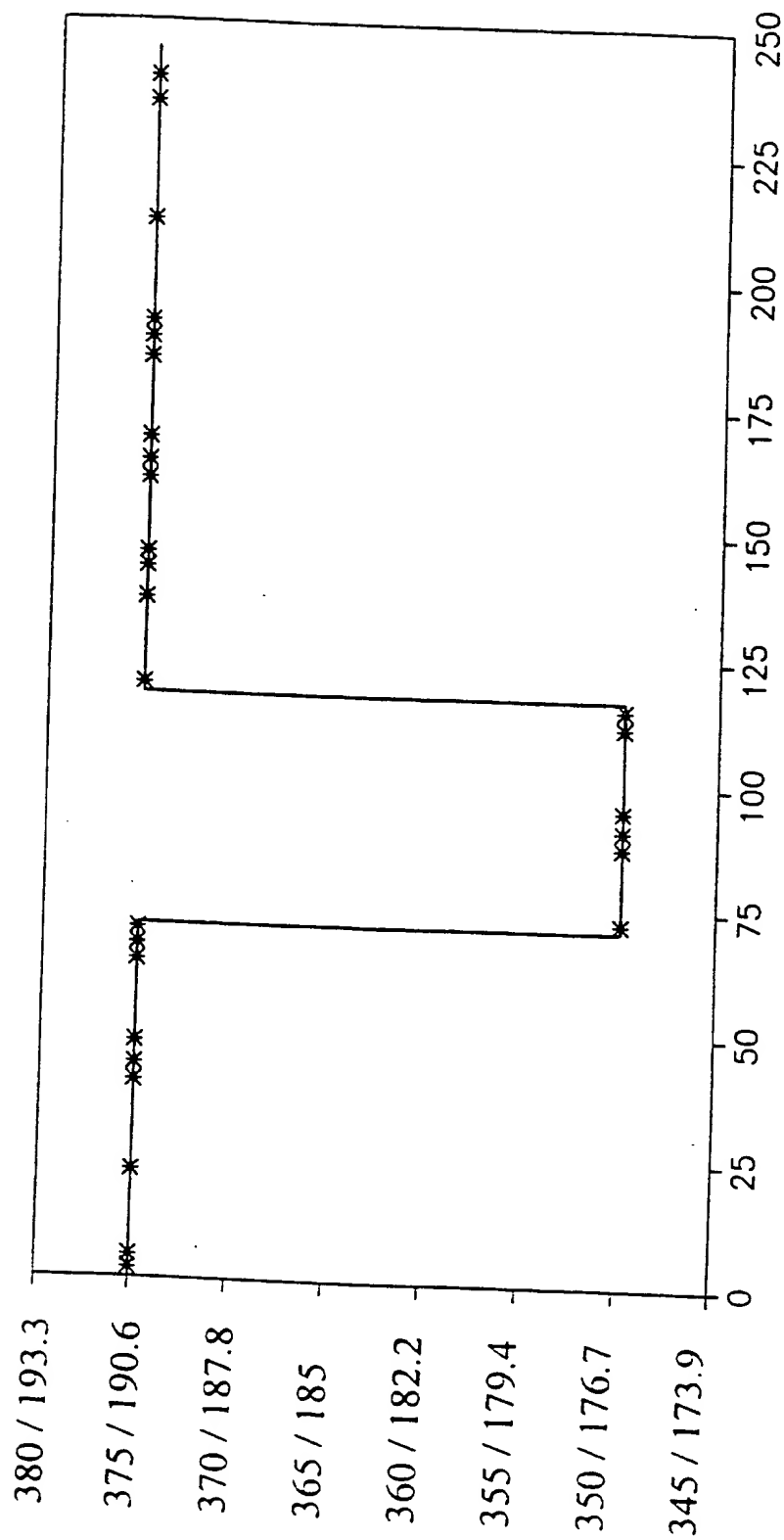


FIG. 7

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/05423

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C10G 29/04, 25/00; F02B 75/12

US CL : 208/208R, 244, 299; 123/1A

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/208R, 244, 299; 123/1A

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 3,485,746 A (SETZER ET AL) 23 December 1969 (23/12/69), See col. 1, lines 20-25 and 69-70, col. 2, lines 35-43 and col. 3, lines 26-45.	1-9 ----- 10-12
Y	US 5,891,538 A (YAMAMOTO ET AL) 06 April 1999 (06/04/99), See column 1, lines 19-22.	10-12
Y,P	US 6,103,103 A (ALEXANDER ET AL) 15 August 2000 (15/08/00), See col. 1, lines 1-25.	10-12
A,P	US 6,129,835 A (LESIEUR ET AL) 10 October 2000 (10/10/00), See entire document.	1-18
A	US 4,336,130 A (MILLER ET AL) 22 June 1982 (22/06/82), See entire document.	1-18

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

01 MAY 2001

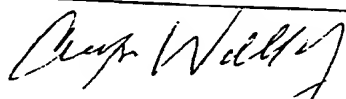
Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/05423

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,419,968 A (LEE) 13 December 1983 (13/12/83), See entire document.	1-18
A	US 4,976,747 A (SZYDLOWSKI ET AL) 11 December 1990 (11/12/90), See entire document.	1-18
A	US 4,347,811 A (LEE) 07 September 1982 (07/09/82), See entire document.	1-18

